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Aromatizing Olefin Metathesis by Ligand Isolation inside a Metal-Organic Framework

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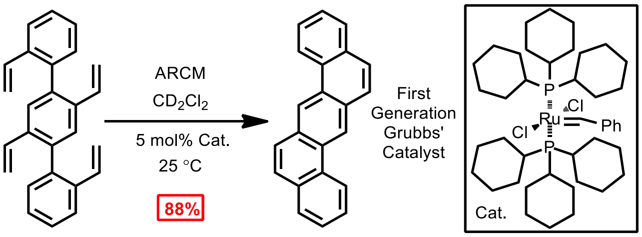
Supporting Information Placeholder

ABSTRACT: The aromatizing ring-closing metathesis has been shown to take place inside an extended porous framework. Employing a combination of solvent-assisted linker exchange and post-synthesis modification using olefin metathesis, the non-interpenetrated **SALEM-14** was formed and converted catalytically into **PAH-MOF-1** with polycyclic aromatic hydrocarbon pillars. The metal-organic framework in **SALEM-14** prevents "intermolecular" olefin metathesis from occurring between the pillars in the presence of the first generation Hoveyda-Grubbs catalyst, while favoring the production of a polycyclic aromatic hydrocarbon, which can be released from the framework under acidic conditions in dimethylsulfoxide.

Recently, metal-organic frameworks (MOFs) have attracted[1] a lot of attention as a unique class of highly adaptive nanoporous materials. The ability of MOFs to incorporate a wide variety of chemical functionality, on account of their easily altered organic struts, has resulted[2] in their exploration for purposes such as gas storage[3], gas separation[4], chemical sensing[5], catalysis[6], and drug delivery[7]. Although *de novo* syntheses of MOFs with a range of different struts, which facilitate the introduction of functionality, have been highly successful, many metal/strut combinations react in quite unpredictable ways[8] and lead to undesirable by-products. In order to overcome these vagaries and achieve the formation of desired frameworks, two alternative synthetic protocols have emerged: they are (i) post-synthesis modification[9] (PSM) and (ii) solvent-assisted linker exchange[10] (SALE). PSM refers to chemical modifications of the organic struts in MOFs to either unmask[11] reactive functionality or introduce[12] functional groups which do not survive (or disrupt) MOF synthesis and has become a common-or-garden approach to generate much sought-after extended frameworks. It is worthy of note that few reports[13] describe C–C bond-forming reactions by PSM. By contrast, SALE allows for the exchange of struts in readily obtainable MOFs to produce[14] extended frameworks with more chemically diverse and useful properties. These two fundamentally different protocols are not mutually exclusive and, employed in concert, can be used to generate metal/strut combinations in MOFs that are not attainable by any other means.

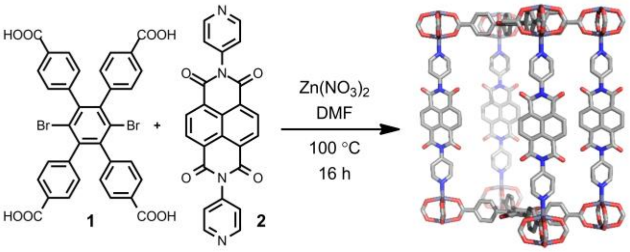
The ability of the olefin metathesis popularized by the extensive use[15] of Grubbs' catalysts[16], to transform molecular structure is both unique and chemically enabling[17]. In addition to the extensive use of this reaction in the fields of polymer chemistry[15b] and materials science[15b], olefin metathesis has been employed in the synthesis of numerous complex small-molecule compounds[15a]. One example[18] of this ubiquitous structural transformation is the generation (Scheme 1) of polycyclic aromatic hydrocarbons (PAHs) from starting materials containing vinyl benzene units. It is known[19] as the aromatizing ring closing metathesis (ARCM); its use inside MOFs would enable the preparation of new extended frameworks employing PSM and would permit the formation of exotic PAHs as isolated linkers in MOFs.

Scheme 1. Use of Grubbs' Catalyst to Make PAHs[18b]



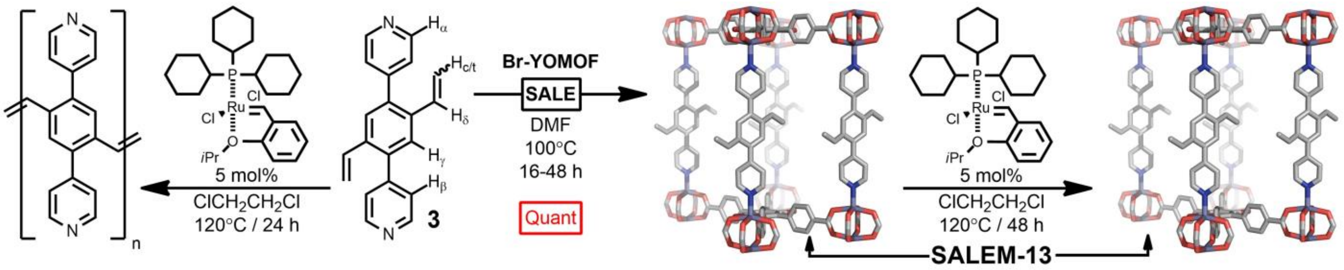
In order to aid and abet the efficient and rapid synthesis of large-pore, non-interpenetrated frameworks containing PAHs, we turned our attention to SALE methodology.[10] We employed the preformed non-interpenetrated framework[20] **Br-YOMOF** which is constructed (Scheme 2) from $Zn(NO_3)_2$ and two organic components – (1) the tetracarboxylic acid ligand **1** (with two bromine atoms[21] on the central phenylene ring to block interpenetration) which forms 2D sheets with Zn^{2+} dimers and (2) the dipyridyl strut **2** which links the 2D sheets by coordinating to the zinc paddlewheel clusters forming perpendicular pillars separating the 2D layers. Following the synthesis of **Br-YOMOF**, the pillars can be exchanged for different dipyridyl linkers employing SALE to provide access to a non-interpenetrated framework without having to resort to *de novo* synthesis.

Scheme 2. Synthesis of Non-Interpenetrated Br-YOMOF



One of the major benefits of doing chemistry inside a highly organized porous material is the unique ability of a rigid, extended framework to site-isolate reactive functional groups and thus prevent unproductive "intermolecular" chemistry. In order to test this concept, we elected to make a strut, which does not, on its own, undergo intramolecular ring-closing metathesis, but instead only

Scheme 3. Synthesis of SALEM-13 and Olefin Metathesis of 3 and SALEM-13



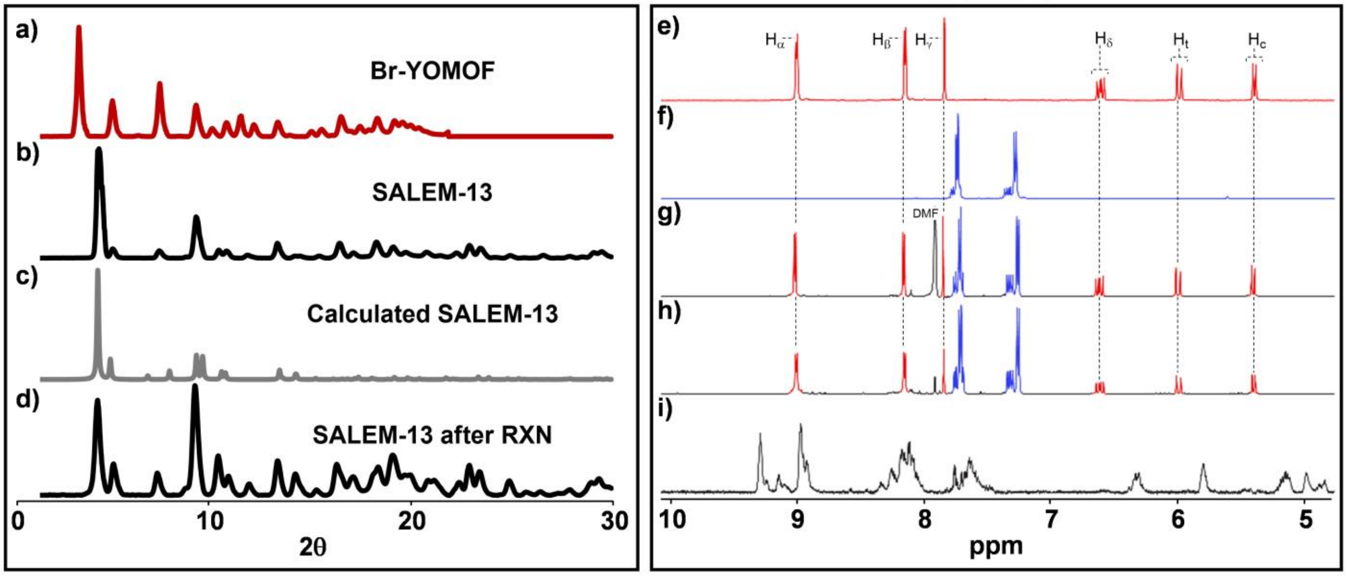


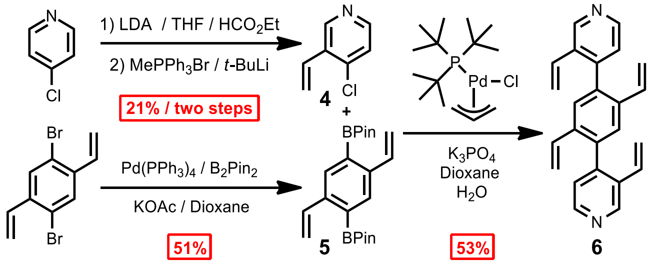
Figure 1. (a) Experimental PXRD of **Br-YOMOF**, (b) experimental PXRD of **SALEM-13** as synthesized, (c) calculated PXRD of **SALEM-13**, and (d) experimental PXRD of **SALEM-13** after olefin metathesis. The partial ^{1}H NMR spectra of (e) the divinyldipyridyl linker **3**, (f) the tetracarboxylic acid ligand **1**, (g) regenerated[22] products (**1** and **3**) from **SALEM-13**, (h) regenerated[22] products (**1** and **3**), following treatment (120°C / 48 h) of **SALEM-13** in DCE with the first generation Hoveyda-Grubbs catalyst, (i) the crude reaction mixture, following treatment (120°C / 24 h) of **3** in DCE with the first generation Hoveyda-Grubbs catalyst. All spectra were recorded in CD_3SOCD_3 containing a few drops of D_2SO_4 at 298 K on a 500 MHz spectrometer.

produces poorly defined polymeric material when exposed to an olefin metathesis catalyst. The divinylpyridyl linker **3** was prepared (see Supplementary Information) and subjected to SALE in order to produce (Scheme 3, Figure 1a,b) **SALEM-13**. The powder X-ray diffraction (PXRD) pattern of **SALEM-13** confirms (Figure 1b) its crystallinity. Furthermore, after the unit cell had been indexed, it was evident that a reduction in its size had taken place during the SALE performed on **Br-YOMOF** to afford **SALEM-13**. The observed [001] peak in **Br-YOMOF** and **SALEM-13** corresponds to a reflection originating from the *c*-axis direction along which the dipyridyl pillars lie. The shift from $2\theta = 3.94$ (Figure 1b) in Br-YOMOF to $2\theta = 4.80$ (Figure 1a) in **SALEM-13** points to the incorporation of a shorter pillar.[23]

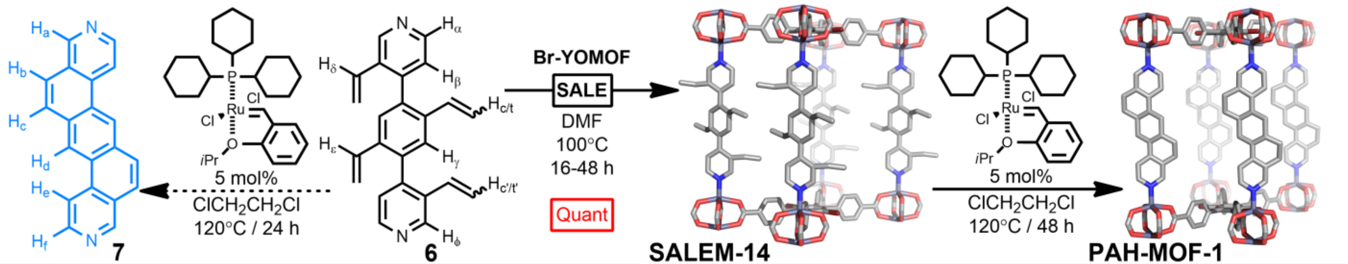
In a dichloroethane (DCE) solution, exposure of **3** to the first generation Hoveyda-Grubbs (HG) catalyst at 120 °C leads to the formation (Scheme 3) of the expected polymeric product as indicated by the broad resonances (Figure 1i) in its ^{1}H NMR spectrum. By contrast, the two vinyl groups in the pillars of the porous extended framework provided by **SALEM-13** revealed *no reactivity at all* (Figure 1e-h), even after prolonged exposure to the same HG catalyst under identical conditions. This observation is consistent with the hypothesis that the MOF site-isolates the potentially reactive olefins, preventing them from undergoing "intermolecular" metathesis. In this knowledge, we undertook the preparation (Scheme 4) of the tetravinyldipyridyl strut **6** which, in principle, should be able to undergo ARCM.

The pyridyl portions of **6** were prepared in two steps from 4-chloropyridine. Its thermodynamic deprotonation using lithium diisopropylamide (LDA), followed by quenching with ethyl formate before carrying out a Wittig reaction with MePPh$_3$Br produced[24] the desired intermediate **4** in 21% over the two steps (Scheme 4). 1,4-Dibromo-2,5-dimethylbenzene was further brominated (NBS, C_6H_6), affording 1,4-dibromo-2,5-bis(bromomethyl)benzene which was treated with PPh$_3$ to generate the diphosphonium bromide before reacting it with paraformaldehyde to give 1,4-dibromo-2,5-divinylbenzene. A subsequent Miyaura borylation afforded[25] the intermediate **5** in 34% yield over the three steps. The tetravinyldipyridyl strut **6** was obtained in 53% yield as a result of carrying out a Suzuki coupling between **4** and **5** using palladium (π-allylchloride)tri(*tert*-butyl)phosphine) as the catalyst[26]. We attempted to prepare (Scheme 5) the PAH **7** in DCE at 120 °C, using

Scheme 4. Synthesis of the Tetravinyldipyridyl Strut 6



Scheme 5. Synthesis of SALEM-14 and Olefin Metathesis of 6 and SALEM-14



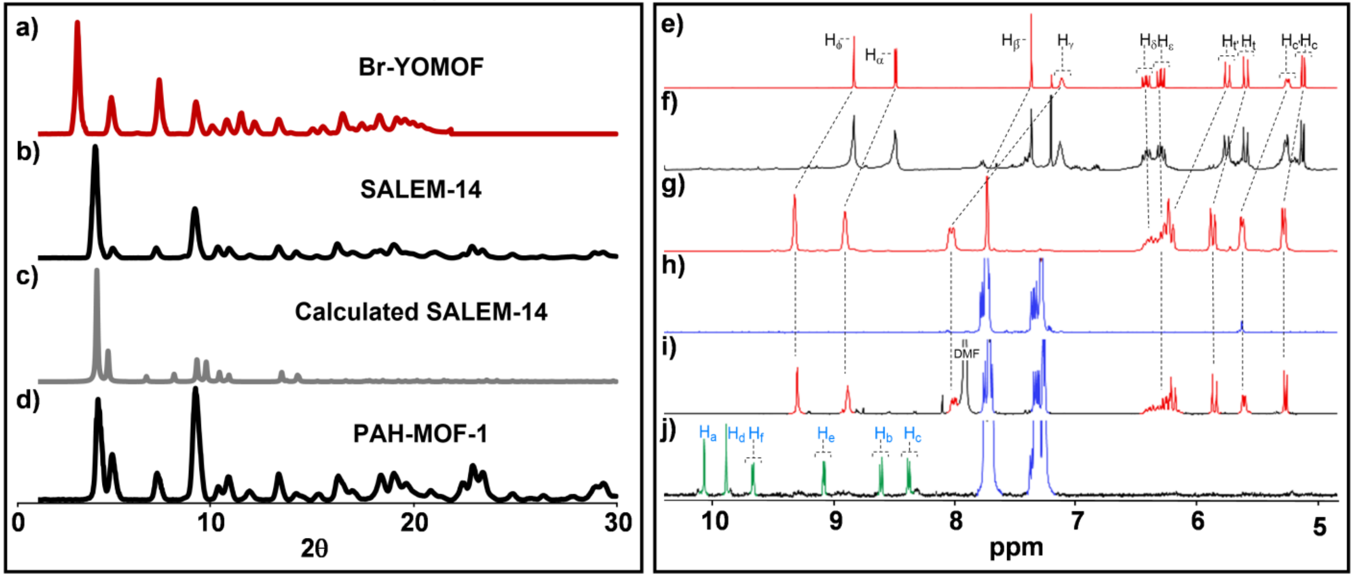


Figure 2. (a) Experimental PXRD of **Br-YOMOF**, (b) experimental PXRD of **SALEM-14** as synthesized, (c) calculated PXRD of **SALEM-14**, and (d) experimental PXRD of **PAH-MOF-1** after ARCM. The partial ^{1}H NMR spectra of (e) the tetravinyldipyridyl linker **6** in $CDCl_3$, (f) the crude reaction mixture from the homogeneous ARCM of **6** following treatment (120°C / 24 h) with the first generation Hoveyda-Grubbs catalyst in $CDCl_3$, showing some broadening of the resonances as a result of some intermolecular polymerization, (g) the tetravinyldipyridyl linker **6** in CD_3SOCD_3 / D_2SO_4, (h) the tetracarboxylic acid ligand **1** in CD_3SOCD_3 / D_2SO_4, (i) regenerated[22] products (**1** and **6**) from **SALEM-14** dissolved in CD_3SOCD_3 / D_2SO_4 and, (j) regenerated[22] products (**1** and **7**) from **PAH-MOF-1** dissolved in CD_3SOCD_3 / D_2SO_4, following treatment (120°C / 48 h) of **SALEM-14** in DCE with the first generation Hoveyda-Grubbs catalyst. All spectra were recorded at 298 K on a 500 MHz spectrometer.

the first generation HG catalyst. The result was only insoluble polymeric material: no **7** could be detected in the reaction mixture. This outcome was hardly surprising as the intermolecular polyermization could be favored under these conditions. It should be noted that ruthenium catalysts employed in metathesis may be poisoned by soft donors, including pyridine.[27] If, however, the tetravinyldipyridyl strut is converted into the pillars of a MOF, then the pyridyl nitrogen atoms in **6** will become strongly coordinated to the dinuclear Zn^{2+} nodes and so will be unable to interfere with the ARCM. Moreover, the extended structure of the MOF prevents the undesired polymerization between tetravinyldipyridyl pillars which characterizes the reaction of **6** in solution.

Thus, employing SALE, strut **6** was incorporated into the **Br-YOMOF** architecture, resulting (Scheme 5, Figure 2a,b) in the production of **SALEM-14** with near quantitative conversion. The SALE reaction was monitored[22] by 1H NMR spectroscopy to ensure complete exchange of the precursor ligand and the new extended structure was analyzed (Figure 2b) by PXRD and shown[28] to be **SALEM-14**, an outcome which was confirmed (see the SI) by single-crystal X-ray structural analysis. **SALEM-14** was rinsed thoroughly with degassed DCE by soaking the crystals in the solvent for 48 h, replacing the solvent every 12 h in order to remove any DMF remaining from the SALE reaction. The formation of the PAH **7** was achieved (Scheme 5) by PSM employing ARCM on the extended porous structure of **SALEM-14** with the first generation HG catalyst in DCE at 120 °C (Figure 2g-j). Within one day, a significant amount of the tetravinyldipyridyl strut **6** had been converted into the PAH strut **7**, as demonstrated by the ^{1}H NMR spectroscopic monitoring procedure[22]. At the end of the second day, **6** had been converted completely into **7** (Figure 2j) inside the extended structure. By contrast, the much larger[29] first generation Grubbs' catalyst was totally ineffective in converting the divinyldipyridyl pillars in **SALEM-14** into the PAH pillars in **PAH-MOF-1** – that is, the mismatch between the size of a catalyst and the dimensions of the pores of a MOF can prevent catalysis from occurring.

In summary, we have demonstrated the use of a suitably-sized ruthenium-based olefin metathesis catalyst inside a metal-organic framework to carry out a solid-state reaction in a post-synthetic fashion that cannot be accomplished in the solution phase. This proof-of-concept investigation, not only demonstrates the synthetic potential of combining post-synthetic modifications with solvent-assisted linker exchange inside the metal-organic framework toolbox, but also establishes the feasibility of performing "intramolecular" chemical transformations where the substrates are prevented from undergoing "intermolecular" reactions in robust, porous extended frameworks. It is clear that these frameworks are capable of exercising size selectivity towards catalysts and presumably also reagents. This kind of solid-state reaction engineering could lead to our being able to functionalize the surfaces and interiors of porous materials in a differentiated manner.

ASSOCIATED CONTENT

Supporting Information

Complete experimental of new compounds and crystallographic data of the prepared MOFs including CIF files. The Supporting InfThis information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(16) Although other catalysts can be used for olefin metathesis, this report will focus on the Ru-based catalysts popularized by Grubbs.

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(21) Although this compound contains some of the mono-Br-mono-NO_2 derivative, it still leads to the formation of the non-interpenetrated MOF.

(22) Crystals isolated from the reaction were washed with DCE, dried, suspended in CD_3SOCD_3 and dissolved using a few drops of D_2SO_4. This procedure destroys the framework and allows the characterization of its constituents by ^{1}H NMR spectroscopy.

(23) Starting form the divinyldipyridyl linker **3** or the tetravinyldipyridyl linker **6**, direct attempts to synthesize **SALEM-13** or **SALEM-14**, respectively, were not successful, validating the SALE approach.

(24) The 4-chloro-3-vinylpyridine intermediate was purified by silica gel plug filtration and carried forward without further purification. This intermediate is volatile and purification simply results in loss of product.

(25) It should be noted that the yield (50%) for the Miyaura borylation is low because of technical issues that had to be confronted during purification of the product. Silica gel chromatography with 0—5% EtOAc/hexanes was not efficient and the product had to be crystallized from hot hexanes.

(26) This catalyst was found to be the most reliable at producing product.

(27) When significant amounts of pyridine are used in relation to the catalyst, reactivity can be impaired. See: (a) Slugovc, C.; Demel, S.; Stelzer, F. *Chem. Commun.* **2002**, 2572; (b) Conrad, J. C.; Fogg, D. E. Curr. *Org. Chem.* **2006**, *10*, 185.

(28) In comparison with the structural transformation from **Br-YOMOF** to **SALEM-13** where $2\theta = 3.94$ (Figure 1a/b), $2\theta = 4.76$ (Figure 2a/b) on going from **Br-YOMOF** to **SALEM-14**, indicating the incorporation of a shorter pillar, an observation which is in good agreement with the predicted PXRD spectrum (Figure 2c).

(29) Marvin was used for analyzing the relative size of the Grubbs' catalysts, Marvin 6.0.2, 2013, ChemAxon (http://www.chemaxon.com): Minimum projection radius was calculated to be: HG1 (6.15 Å) < HG2 (6.68 Å) < G2 (7.50 Å) < G1 (7.89 Å).

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